NONAROMATIC ANALOGS OF HINDERED BENZILS AND THEIR DERIVATIVES

BY
JAMES ADOLPH ROBERTSON
B.A., Park College, 1937
M.S., University of Oklahoma, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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Introduction

When it was discovered that diarylacetylene glycols were produced by 1,4 addition of hydrogen to hindered benzils,[1,2] a study of the factors contributing to the stability of the new type of enediol was begun. One problem was to eliminate the possible stabilizing influence of conjugation with aromatic radicals. This investigation deals with the chemical properties of analogous compounds containing one or more aliphatic substituents.

Discussion of Results

2,6-Dimethylhexahydrobenzoic acid was chosen as the compound from which the synthesis of an aliphatic enediol would be attempted. One form of the acid was prepared by reducing 2,6-dimethylbenzoic acid with hydrogen in the presence of Raney nickel. 2,6-Dimethylhexahydrozenzoyl chloride and ethyl 2,6-dimethylhexahydrobenzoate were reduced bimolecularly with the binary mixture ($Mg\text{-}MgI_2$) and sodium, respectively. The products from both reductions were 2,6-dimethylhexahydrobenzil and the corresponding acyloin. The latter was isolated, and formed an acetate. The diketone was reduced to the acyloin at high pressures, using a copper chromite catalyst, but failed to absorb hydrogen in the presence of platinum at atmospheric pressure. No enediol was detected.

Condensation of *t*-butylglyoxal with mesitylene gave both the known pivalylmesitylcarbinol[3] and the previously undescribed isomer, *t*-butylmesitoylcarbinol. The latter acyloin was reduced to the corresponding ethylene glycol, oxidized to the diketone and converted into its isomer, pivalylmesitylcarbinol, by treatment with sodium ethoxide. The opposite transformation failed to occur under similar conditions.

t-Butyl mesityl diketone formed a mono-oxime, and was reduced with hydrogen and a platinum catalyst to an enediol in solution which isomerized to pivalylmesitylcarbinol. Treat-

ment of the diketone with methylmagnesium iodide resulted in the formation of the two isomeric ketols. Cleavage of the lower melting ketol with sulfuric acid produced mesitylene and pinacolone. The higher melting ketol was dehydrated with the same reagent to give *t*-butyl ∝-mesitylvinyl ketone, which in turn absorbed one mole of hydrogen in the presence of platinum. The resulting vinyl alcohol was isomerized to the keto form and was converted to a peroxide derivative.

t-Butylmesitylethylene glycol was obtained from the reduction of *t*-butylmesitoylcarbinol with hydrogen and a copper chromite catalyst, and was dehydrated with sulfuric acid to give pivalylmesitylmethane. The latter compound formed an oxime and did not enolize in the presence of methylmagnesium iodide.

Pivalylmesitylene and mesitil were prepared, and each was treated with methylmagnesium iodide. The former ketone was recovered completely unchanged. Contrary to a previous report,[4] mesitil reacted with the Grignard reagent to some extent, producing small amounts of mesitoin.

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VITA

The author was born in St. Louis, Missouri on June 4, 1916. He attended the public schools of that city and graduated from Grover Cleveland High School in June, 1933. The following four years were spent at Park College, Parkville, Missouri, from which he received a B. A. degree in June, 1937. That Fall, he enrolled in the Graduate School of the University of Oklahoma where he served for two years as a Graduate Assistant in Chemistry and was given a M. S. degree in June, 1939. Since that time, the author has been engaged in graduate work in Chemistry at the University of Illinois, where he held a Graduate Assistantship during the years 1940-1941 and a University Fellowship in 1941-1942.

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